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NONEQUILIBRIUM DISCLINATIONS IN THE CARBONACEOUS
MESOPHASE(U) AEROSPACE CORP EL SEGUNDO CA MATERIALS
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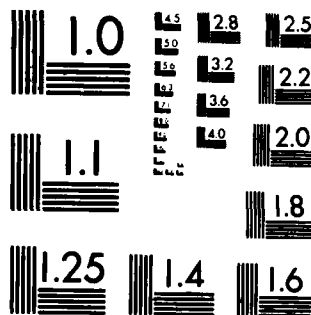
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Prepared for
SPACE DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009


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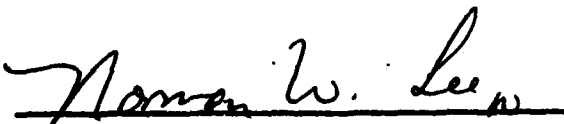
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Steven G. Hancock, 2nd Lt, USAF
Project Officer


David T. Newell, Lt Col, USAF
Actg Dir, Space Systems Technology

FOR THE COMMANDER


Norman W. Lee, Jr., Colonel, USAF
Commander, Det 1, AFSTC

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The behavior of carbonaceous mesophase in the liquid crystalline state has been observed directly by polarized light on the free surface of a petroleum pitch during pyrolysis. The present work focuses attention on the reactions between various disclinations, and primarily on the spontaneous generation of new disclinations from compressed folds in the mesophase layers. Specimens quenched from critical stages in such reactions reveal that structures of freshly formed disclinations can be distorted appreciably from the equilibrium structures of relaxed disclinations.		

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I. INTRODUCTION

The following technical discussion was originally written as a Letter to the Editor of Carbon and is prepared as a technical report in accordance with Aerospace practice. The style is terse, as required for a letter to the editor, so that some prefatory remarks may be helpful for readers not conversant with the special terminology of liquid crystals and the carbonaceous mesophase.

Graphitic materials differ from other structural materials in being formed by a liquid crystal (mesophase) transformation¹ and therefore contain the microstructural features known as disclinations, which are inherent to liquid crystals.² The quenching hot-stage microscope has proven to be a valuable tool for obtaining a qualitative understanding of the carbonaceous mesophase and of the disclination interactions that occur within that anisotropic liquid.^{3,4}

In the discussion, we emphasize how the disclination structures are similar in both carbonaceous mesophase and conventional liquid crystals; we then point out a difference important to materials such as graphite and mesophase pitch fibers, namely, that their disclination structures have usually been subjected to strong deformation stresses as the mesophase hardens. Thus, the microstructures of such practical spacecraft materials as rocket nozzles, nose cones, and reinforcing fibers for structural members may include disclinations appreciably deformed from the equilibrium structures characteristic of fluid liquid crystals. We currently employ the concepts of mesophase deformation and nonequilibrium disclinations to construct reasonable working models of the mechanical behavior of the high-modulus carbon fibers⁵ favored for dimensionally stable spacecraft components.



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A

II. TECHNICAL DISCUSSION

Friedel's classic work on liquid crystals⁶ summarizes his observations of structural reactions within nematic liquids in a table similar to Table 1. The symbols $\pm 2\pi$ refer to crosses in the polarized-light extinction contours (noyaux in Friedel's terminology), and the symbols $\pm\pi$ refer to nodes (demi-noyaux); the signs \pm indicate the direction of the extinction contours when the line of polarization of the incident light is rotated.² In current terminology, these singular points are liquid crystal disclinations having the equilibrium structures⁷ represented in Fig. 1.

We have used a quenching hot-stage microscope to observe similar disclination reactions in the carbonaceous mesophase.³ The quenching capability froze disclination structures at critical stages for detailed study. A 32 \times objective with 6-mm working distance proved adequate for resolving orientational fluctuations similar to those Friedel⁶ observed in conventional nematic liquid crystals. Such fluctuations are most readily seen in a freshly formed, very fluid mesophase as a fine local flickering in the darkness of polarized-light extinction contours.

The micrographic sequence of Fig. 2 illustrates five disclination reactions observed within a 2-min period during pyrolysis of Ashland A240 petroleum pitch. In region A, two 2π disclinations of opposite sign appear to be spontaneously generated by a "pinch-off" reaction. These disclinations then separate, and the right-hand disclination moves toward region B, where it annihilates another 2π disclination. In region C, the reaction is

$$(+\pi) + (-2\pi) \rightarrow (-\pi)$$

The disclination signs were identified by rotating the line of polarization. These reactions have been observed to take place in both forward and reverse directions, suggesting that the energies of disclination structures are small relative to the work of deformation by mechanisms such as bubble percolation. As pyrolysis is continued, the disclination reactions slow well before the mesophase loses its deformability.

The pinch-off reaction was examined further by quenching a specimen while the new disclinations were still moving apart (Fig. 3). At that point, the extinction contours were also rotating about the centers of the moving crosses, indicating internal rearrangements of the disclination structures immediately after the reaction. The specimen fortuitously included another region of compressed contours in which the pinch-off reaction appeared ready to occur (Fig. 4). The structural sketches indicate that this reaction consists of the sudden replacement of compressed folds by undistorted mesophase layers. The folds are so tightly compressed that disclination generation could be nucleated by an orientational fluctuation.

Although the wavelength of light limits the structural detail that can be derived by the polarized-light techniques used here, the freshly formed disclinations appear to have nonequilibrium structures of the type sketched in Fig. 5. Such nonequilibrium disclination structures may be expected in mesophase products whenever the mesophase is being deformed as it hardens, as, for example, in the spinning of mesophase fiber.⁷

TABLE 1. DISCLINATION INTERACTIONS IN NEMATIC LIQUID CRYSTALS

$(+2\pi) + (-2\pi) \rightleftharpoons 0$	}	Annihilation and formation reactions
$(+\pi) + (-\pi) \rightleftharpoons 0$		
$(+2\pi) + (-\pi) \rightleftharpoons (+\pi)$	}	Reactions between disclinations of different strengths
$(-2\pi) + (+\pi) \rightleftharpoons (-\pi)$		
$(+\pi) + (+\pi) \rightleftharpoons (+2\pi)$	}	Combination and dissociation reactions
$(-\pi) + (-\pi) \rightleftharpoons (-2\pi)$		

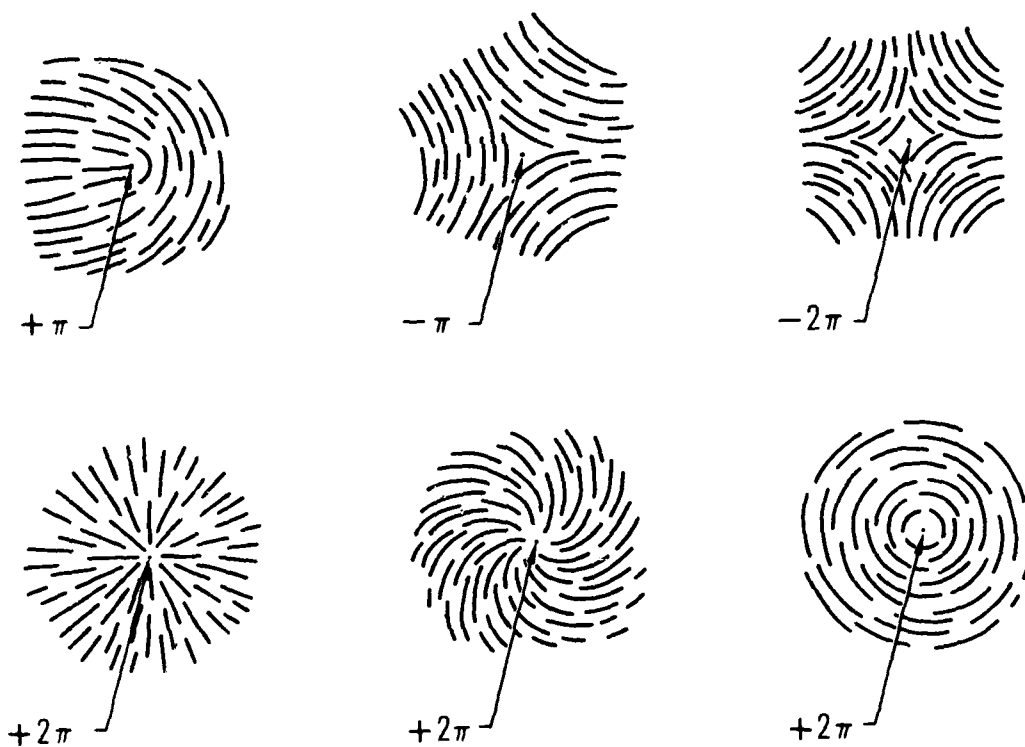


Fig. 1. Wedge disclinations in a liquid crystal. After Frank.⁷



Fig. 2. Disclination interactions observed by crossed polarizers on the free surface of a petroleum pitch pyrolyzed to 440°C: region A, spontaneous generation of 2π disclinations; region B, annihilation of 2π disclinations; region C, reaction $(+\pi) + (-2\pi) \rightarrow (-\pi)$. Letters a through f indicate sequence.

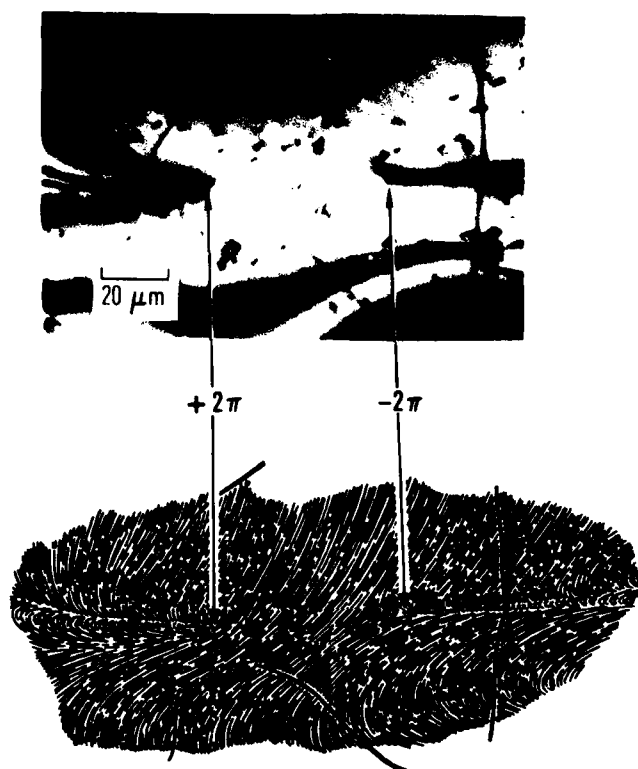


Fig. 3. Two 2π disclinations formed by pinch-off reaction. Crossed polarizers. Structural sketch by polarized-light mapping² of quenched specimen.

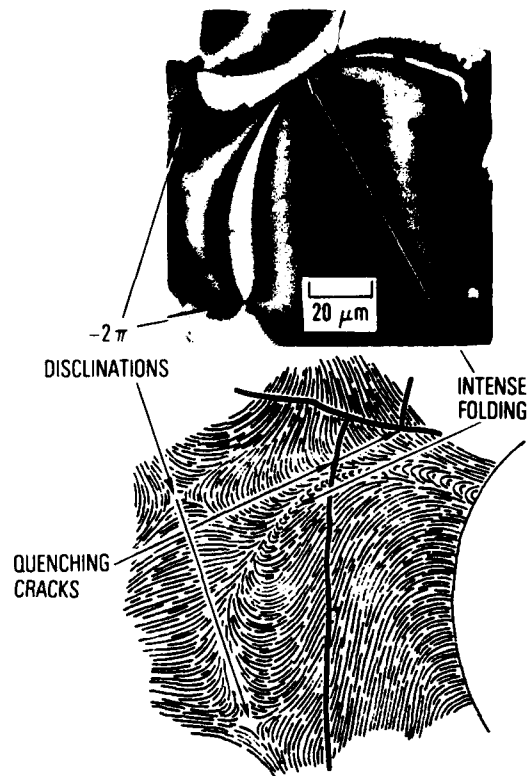


Fig. 4. Compressed folding of type observed prior to a pinch-off reaction. Crossed polarizers.

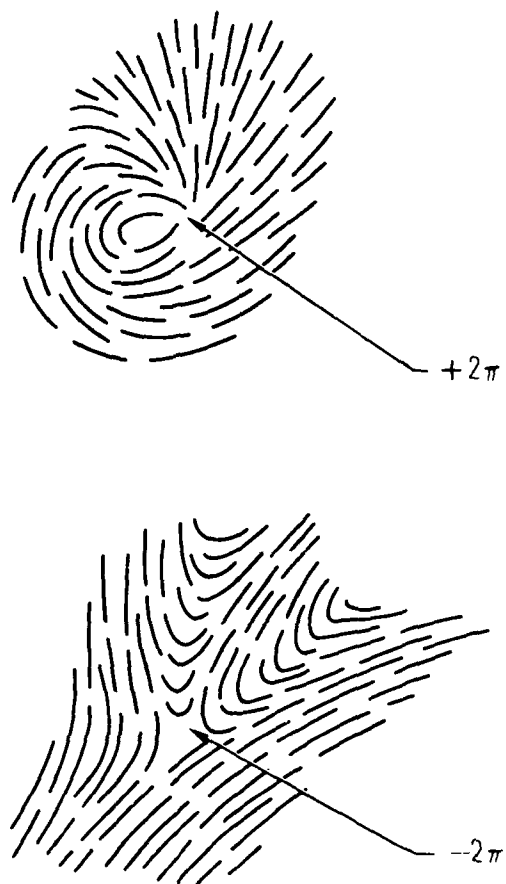


Fig. 5. Nonequilibrium disclinations as freshly formed in the carbonaceous mesophase.

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